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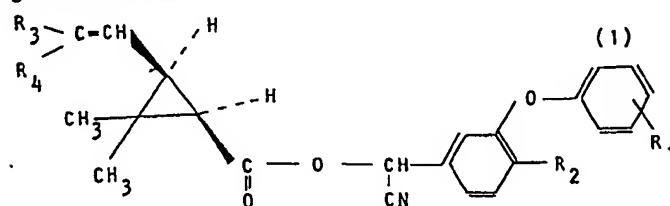
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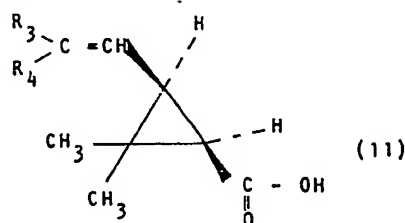
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(54) Preparation of cyanobenzyl cyclopropane carboxylates.

(57) A method for preparing a pyrethroid insecticide of general formula:

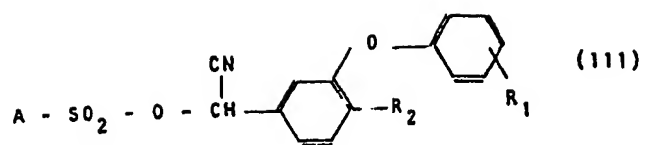


wherein the two hydrogen atoms on the cyclopropane ring are in the *cis*- configuration, in which an acid of formula:



is neutralised with a water-soluble base and then reacted in the presence of a phase-transfer catalyst with a solution in a substantially water-immiscible organic solvent of an alpha-cyanobenzyl aryl sulphonate of formula:

./...



the substituents in the formulae having the following meanings; A represents an optionally substituted aryl group;  $R_1$  and  $R_2$  represent hydrogen or halogen; and  $R_3$  and  $R_4$  represent chlorine, bromine, or methyl.

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"PREPARATION OF CYANOBENZYL CYCLOPROPANE CARBOXYLATES"

This invention relates to the preparation of synthetic pyrethroid insecticide esters by reacting a cyanobenzyl arylsul-  
5 phonate with a cyclopropane carboxylic acid.

U.K. Patent Specification No. 1,540,632 discloses a process for preparing synthetic pyrethroid insecticide esters containing a 3-substituted alpha-cyanobenzyl group as the alcohol moiety wherein a 3-substituted benzaldehyde (e.g. 3-phenoxybenzaldehyde)  
10 is reacted with the appropriate acyl chloride or bromide (e.g. 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarbonyl chloride) in the presence of water, a water soluble cyanide, a substantially water-immiscible aprotic solvent and a phase-transfer catalyst.

U.K. Patent Specification No. 1,559,799 discloses a process  
15 for preparing similar synthetic pyrethroid insecticide esters wherein the appropriate acid (e.g. 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid) is neutralised with a water-soluble base and then reacted with a solution in a substantially water-immiscible organic solvent of an alpha-cyano-3-phenoxy-  
20 benzyl halide in the presence of a phase-transfer catalyst.

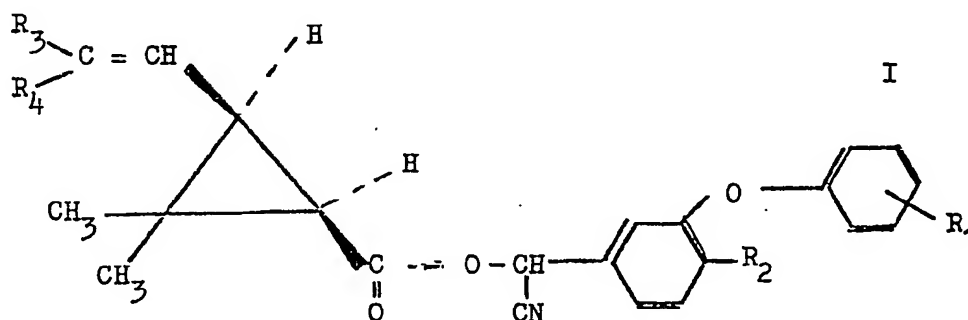
Synthetic pyrethroid insecticide esters which are alpha-cyano-3-phenoxybenzyl 3-(2,2-di-substituted vinyl)-2,2-dimethylcyclopropanecarboxylates have eight possible isomers, since the cyclopropane ring of the acid moiety contains two centres of  
25 asymmetry and a third centre of asymmetry exists in the alcohol moiety. In general, superior pesticidal activity resides among the compounds having cis-configuration about the cyclopropane

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ring, as disclosed by Itaya et al in "Synthetic Pyrethroids", ACS Symposium Series 42, Pages 45 to 54, and the isomer which has the greatest pesticidal activity is generally that isomer which is conveniently designated the 1R cis S- isomer, 1R cis-designating configuration in the acid moiety and S-designating configuration in the alcohol moiety, as described by Elliott et al in Nature, Vol. 248, Pages 710 and 711 (1974).

Although the processes of the above two U.K. Patents both give excellent results, that of U.K. Patent Specification No. 1,540,632 is economically more attractive since it employs as starting material the commercially available 3-phenoxybenzaldehyde. When cis-alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate is prepared from pure cis- 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid by the process of U.K. Patent Specification No. 1,540,632, it has been found that the product is typically 95% by weight pure ester which contains the cis/trans-isomers in 95:5 ratio by weight. If this product is used directly in the process described in U.K. Patent Specification No. 2075011, the maximum yield has been found to be 65% by weight of 95% pure 1:1 mixture of 1R cis, S- and 1S cis R- isomers of the ester.

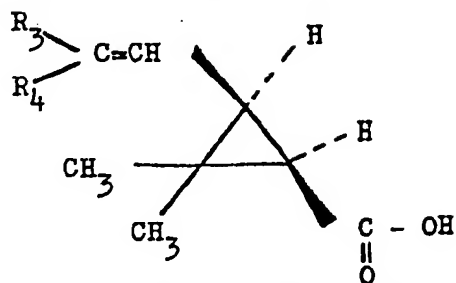
The present invention provides a synthetic route to such pyrethroid insecticides which facilitates the production in good yields of the more active cis isomer(s) of the general formula:-



wherein the two hydrogen atoms on the cyclopropane ring are in

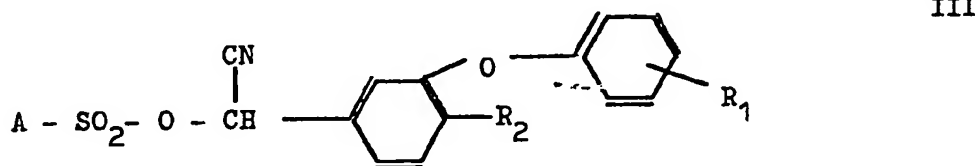
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the cis- configuration, characterised in that an acid of formula



is neutralised with a water-soluble base and then reacted in the presence of a phase-transfer catalyst with a solution in a substantially water-immiscible organic solvent of an alpha-cyano-

5 benzyl aryl sulphonate of formula:



the substituents in the formulae having the following meanings; A represents an optionally substituted aryl group; each of  $R_1$  and

10  $R_2$  independently represents a hydrogen or halogen atom; and each of  $R_3$  and  $R_4$  independently represents a chlorine or bromine atom or a methyl group.

A may be, for example, a phenyl group substituted by one or more substituents independently selected from halogen atoms,

15 nitro groups, and alkyl and alkoxy groups preferably containing 1 to 6 carbon atoms and optionally halogenated, suitably by fluorine, chlorine or bromine, and is conveniently a phenyl group substituted by one or more methyl groups. Advantageously A is a tolyl group.

20 Advantageously  $R_1$  is hydrogen or bromine and  $R_2$  is hydrogen or fluorine, at least one of  $R_1$  and  $R_2$  being hydrogen. Preferably  $R_2$  and  $R_2$  are both hydrogen. Preferably  $R_3$  and  $R_4$  are both chlorine.

Using a neutralised acid of formula II in reaction with an

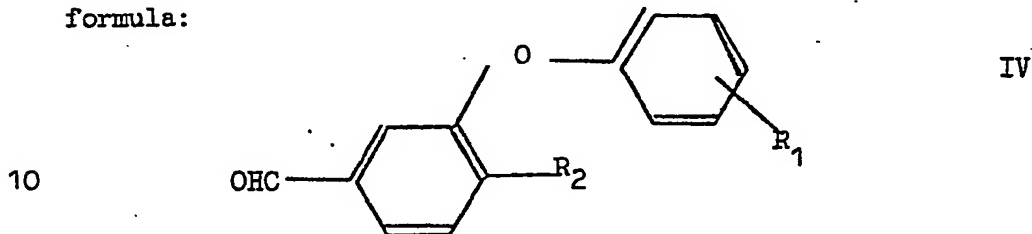
25 alpha-cyanobenzyl arylsulphonate of formula III it has been found

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possible to retain the cis-configuration substantially completely in preparing the pyrethroid insecticide of formula I.

The acid of formula II may conveniently be neutralised using a water-soluble inorganic base such as sodium or potassium bicarbonate, carbonate or hydroxide. Advantageously the inorganic base is sodium bicarbonate or potassium bicarbonate.

Alpha-cyanobenzyl arylsulphonates of formula III may be prepared by a process which comprises reacting a benzaldehyde of formula:



wherein  $R_1$  and  $R_2$  are as defined above, with an alkali metal cyanide and an arylsulphonyl halide of formula  $A-SO_2-Hal$ , wherein  $A$  is as defined above and  $Hal$  is fluorine, bromine or preferably, chlorine.

15 This process is conveniently carried out in the presence of water, a substantially water-immiscible organic solvent and a phase transfer catalyst. Potassium and, especially, sodium cyanides are the preferred alkali metal cyanides.

The phase-transfer catalyst may be any reagent which will  
 20 accelerate interphase reactions in aqueous/organic two-phase systems, the most convenient such catalysts including quaternary ammonium and phosphonium compounds. Generally economic considerations make it preferable to use quaternary ammonium compounds. Examples of suitable quaternary ammonium compounds include tetra  
 25 alkylammonium halides, for example, tetra-n-butylammonium bromide, tetra-n-butylammonium chloride, cetyltrimethylammonium bromide and methyltri( $C_{8-10}$  alkyl)ammonium chlorides, and also methyltri-2-methylphenylammonium chloride. Alternatively, the macrocyclic polyethers known as "crown ethers" may be utilized as phase  
 30 transfer catalyst. These compounds, together with their prepa-

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ration, are described in the literature, for example in Tetra-  
hedron Letters No. 18 (1972) pp. 1793-1796, and are commonly  
designated by reference to the total number of atoms forming the  
macrocyclic ring together with the number of oxygen atoms in that  
ring. Thus the macrocyclic polyether whose formal chemical name  
is 1,4,7,10,13,16-hexaoxacyclooctadecane is designated as "18-  
crown-6". Other types of compound which may be used as the  
phase-transfer catalyst include quaternary ammonium anion ex-  
change resins (suitably in the hydroxyl form).

The concentration of catalyst used may vary widely, but at  
low concentrations (e.g. 1 mole % or less) a higher reaction  
temperature is required to complete the esterification reaction  
within an acceptable period of time whilst the use of higher  
concentrations (e.g. above 10 mole %) naturally increases the  
cost of the catalyst required to produce a given quantity of  
ester. For example, the use of 5 mole % of catalyst at 65-70°C  
will lead to a 20-30 fold reduction in reaction time as compared  
with the same reagent concentrations at room temperature, and  
reduction of the catalyst concentration to 1 mole % increases the  
reaction time 2-3 fold. Thus, the choice of reaction temperature  
and catalyst concentration are mutually interdependent, and in  
any individual instance will depend on the local economic factors.  
Those skilled in the art will appreciate that the nature of the  
reaction vessel and the stirring rate are other factors to be  
taken into account in determining optimum reaction conditions.

Preferred substantially water-immiscible organic solvents in  
either the preparation of the compounds of formula I or the  
cyanobenzyl arylsulphonate precursors of formula III include  
benzene, toluene, petroleum ethers, xylenes, trimethylbenzene,  
carbon tetrachloride and kerosene.

The invention is illustrated in the following examples:

#### EXAMPLE 1

##### A) Preparation of alpha-cyano-3-phenoxybenzyl p-toluene sulphonate

A solution of 3-phenoxybenzaldehyde (198g, 1.0M) and p-

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toluenesulphonyl chloride (190.5g, 1.0M) in toluene (200ml) was stirred under nitrogen and cooled to 0°C. A solution of sodium cyanide (51g, 1.04M) and tetra-n-butylammonium bromide (1.5g, 0.005M) in water (200ml) was added dropwise over 45 minutes.

5 After stirring for a further hour at 0 to 5°C, the organic phase was separated off and washed with water (2 x 100ml). The toluene was evaporated off leaving an orange oil (395g) which on crystallisation from ethanol (600ml) at 15°C yielded alpha-cyano-3-phenoxybenzyl p-toluenesulphonate as a pale cream crystalline  
10 solid (341g, 89.9%) m.p. 56-57.5°C.

B) Preparation of cis-alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate from alpha-cyano-3-phenoxybenzyl p-toluene sulphonate.

Cis- 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane car-  
15 boxylic acid (199g, 0.95M) was added to a solution of potassium carbonate (65.6g, 0.475M) in water (450ml). Toluene (900ml), tetra-n-butylammonium bromide (13.5g, 0.05M) and alpha-cyano-3-phenoxybenzyl p-toluenesulphonate (341g, 0.9M; prepared as described in A above) were added to the stirred mixture which was  
20 then heated at 70°C for 3 hours. The mixture was cooled to ambient temperature and the organic phase was separated off, washed with aqueous potassium carbonate solution (2 x 200ml) and water (2 x 200ml), evaporated and degassed under vacuum to leave  
25 cis-alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethyl- cyclopropanecarboxylate as a pale amber oil (364g, 97.3%), containing less than 1% trans- isomers.

The purity of the cis-alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate was confirmed by subjection to the process described in U.K. Patent  
30 Specification No. 2,075011. Thus the amber oil (364g) was dissolved in triethylamine (550ml) and stirred at 15°C. The precipitate which crystallised out was filtered off, washed with cold triethylamine (50ml) and cold hexane (100 ml) and dried to give 268g of white crystalline solid, m.p. 83-  
35 84.5°C, containing 95% by weight of a 1:1 mixture of the 1R cis

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S- and 1S cis R- isomers of alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate.

The solvent was evaporated from the filtrate and the residue (95g) was dissolved in triethylamine (150ml) and treated as above  
5 to give a further 41.4g of white crystalline solid, m.p. 82-84°C, containing 95% by weight of a 1:1 mixture of the 1R cis S- and 1S cis R- isomers of alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate.

Thus, in two treatment steps a 95% pure 1:1 mixture of 1R  
10 cis S- and 1S cis R-isomers of alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate was obtained in 85% yield based on the weight of the amber oil.

#### EXAMPLE 2

Cis- 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane car-  
15 boxylic acid (1680g, 8.04M) was added to a solution of potassium carbonate (555g, 4.02M) in water (3800 ml). Toluene (7600 ml), tetra-n-butylammonium bromide (115g, 0.4M) and alpha-cyano-3-phenoxybenzyl p-toluenesulphonate (2902g, 7.65M; prepared as in Example 1(A) above) were added to the stirred mixture which was  
20 then heated at 70°C for 5 hours. The mixture was cooled to ambient temperature and the organic phase was separated off, washed twice with aqueous potassium carbonate solution and twice with water, evaporated and degassed under vacuum to leave cis-alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethyl-  
25 cyclopropanecarboxylate as a yellow oil (3130g, 99%), containing less than 1% trans- isomers.

This yellow oil (3130g) was dissolved in triethylamine (4650 ml) and stirred at 15°C for 24 hours. The precipitate which crystallised out was filtered off, washed with cold triethyl-  
30 amine (750 ml) and cold hexane (1000 ml) and dried to give 173g of white crystalline solid, m.p. 81-83°C, containing 94% by weight of a 1:1 mixture of the 1R cis S- and 1S cis R- isomers of alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate.

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The solvent was evaporated from the filtrate and the residue was dissolved in triethylamine (2000 ml) and treated as above to give a further 864g of white crystalline solid, m.p. 81.5-83.5°C, containing 94% by weight of a 1:1 mixture of the 1R cis S- and 1S cis R- isomers of alpha-cyano-3-phenoxybenzyl 3-(2,2-dichloro-  
5 vinyl)-2,2-dimethylcyclopropanecarboxylate.

Concentration of the filtrate and stirring at 15°C for 48 hours enabled a further 96g of white crystalline solid, m.p. 82.5-84°C, containing 95% by weight of a 1:1 mixture of the 1R cis S- and 1S cis R- isomers of alpha-cyano-3-phenoxybenzyl 3-  
10 (2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, to be obtained.

Thus in three treatment steps a 94% pure 1:1 mixture of 1R cis S- and 1S cis R- isomers of alpha-cyano-3-phenoxybenzyl 3-  
15 (2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate was obtained in 86.2% yield based on the weight of the yellow oil.

EXAMPLES 3 to 6

Cis- 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid (22g, 0.105M) was added to a solution of an inorganic  
20 base in water (50 ml). Toluene (100 ml), tetra-n-butylammonium bromide (1.6g, 5 mole % based on the cyclopropane carboxylic acid) and alpha-cyano-3-phenoxybenzyl p-toluenesulphonate (37.9g, 0.1M) were added to the stirred mixture which was then heated at 40-45°C for 24 hours. The reaction mixture was then treated as  
25 in Example 1 to yield cis- alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate as a pale amber oil containing less than 1% trans- isomers.

The bases, their quantities and the yields obtained are given in Table I following.

9.

Table I

Base	quantity of base	Yield (g)
sodium hydroxide	4.2g, 0.105M	39.4g
potassium carbonate	7.25g, 0.0525M	41.0g
potassium carbonate	14.5g, 0.105M	38.75g
sodium bicarbonate	8.82g, 0.105M	41.3g

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EXAMPLES 7 to 9

Following the procedure of Example 6 (i.e. sodium bicarbonate as base), but using different phase-transfer catalysts (1.6g in each case) and stirring at 40-45°C until reaction was  
5 complete (as determined by thin-layer chromatography), gave cis alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate as a pale amber oil containing less than 1% trans- isomers, as indicated in the following Table II.

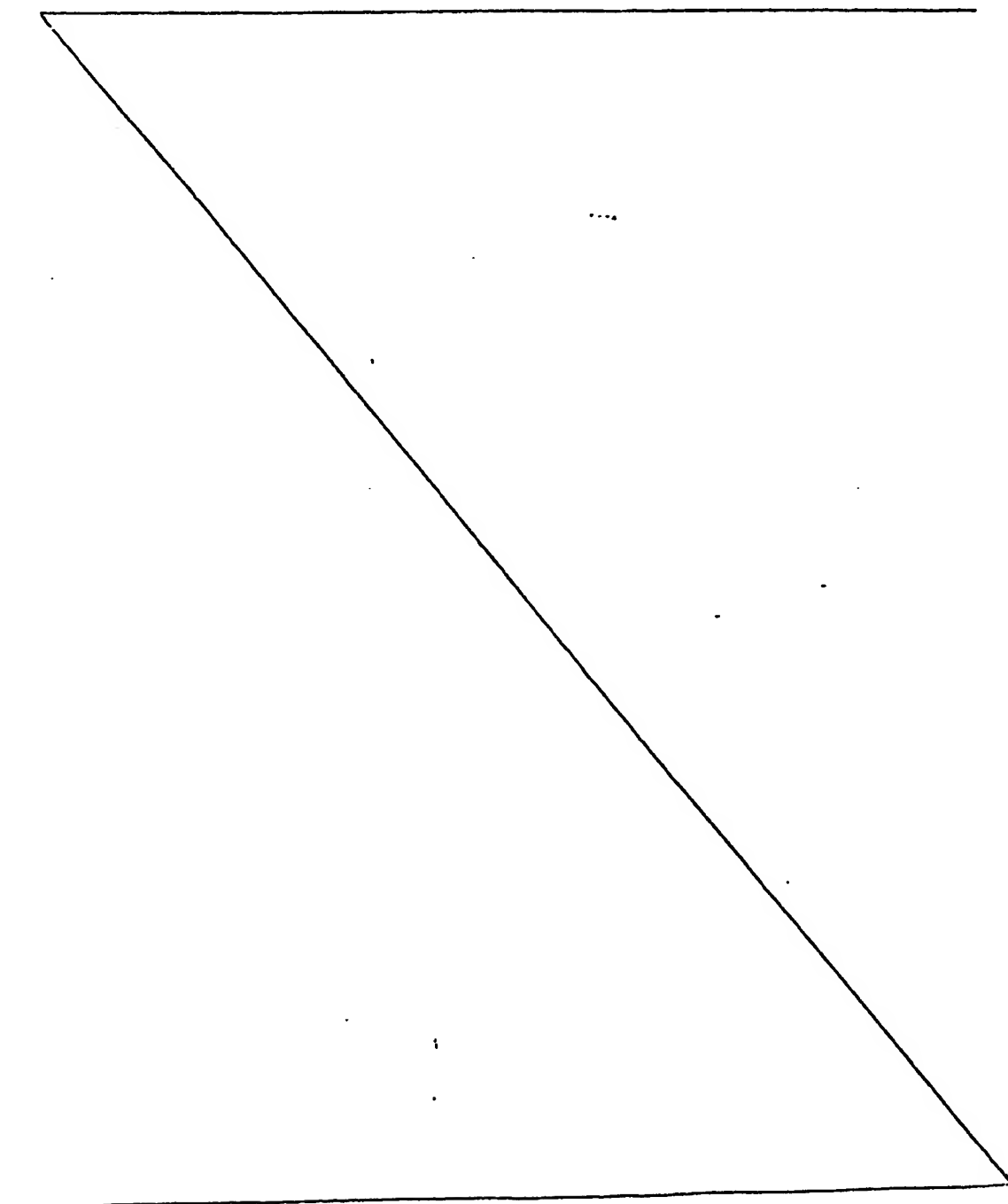


Table II

Phase-transfer catalyst	Reaction time (hrs)	Yield (g)
ADGEN 464 (Trade Mark)	30 hrs	41.7g
Cetyltrimethylammonium bromide	50 hrs	40.85g
Tetrabutylammonium bromide	22 hrs	41.0g

ADGEN 464 (ex Aldrich Chemical Company) is a mixture of methyltri(C<sub>8-10</sub> alkyl)ammonium chlorides,  $\eta_D^{20}$  1.4665.

12.

EXAMPLES 10 and 11

Following the procedure of Example 9 but using carbon tetrachloride (100 ml) in place of toluene, and using tetrabutylammonium bromide (1.6g) as catalyst, gave cis-alpha-cyano-3-phenoxymethyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate as a pale amber oil containing less than 1% trans-isomers, as indicated in the following Table III.

Table III

Reaction temperature (°C)	Reaction time (hrs)	Yield (g)
40-45°C	20 hours	41.25g
63-66°C	3 hours	39.9g

13.

Comparative Example

Cis-alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate was prepared by the process of UK Patent Specification No. 1,540,632 as follows. A solution of  
5 sodium cyanide (980g, 20M) and tetrabutylammonium bromide (0.5g, 0.01M) in water (3835 ml) was added to a stirred mixture of 3-phenoxybenzaldehyde (3305g, 16.69M) and cis -3-(2,2-dichloro-  
vinyl)-2,2-dimethylcyclopropanecarbonyl chloride in toluene (17 litres) over a period of 3 hours whilst maintaining the temper-  
10 ature of the mixture in the range 10° to 12°C.

The mixture was stirred for 7 hours, more tetrabutylammonium bromide (11g, 0.22M) was added and the mixture was stirred overnight. The aqueous layer was removed from the mixture and the organic phase was washed successively with 5% aqueous potassium  
15 carbonate solution and with demineralised water and was evaporated under reduced pressure to yield alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (7.0kg) as a pale amber oil which was shown by high-performance liquid chromatography to contain 95% cis-isomers: 5% trans- isomers  
20 (w/w).

This 95:5 mixture of cis- and trans- isomers was subjected to the process described in UK Patent Application No. 8112344. Thus the amber oil was dissolved in triethylamine (10.5 litres) and stirred at 15°C for 5 days. The crystalline precipitate  
25 which formed was filtered off, washed with cold triethylamine and cold hexane and dried to give 4.5kg of white crystalline solid, m.p. 83.5-85.5°C, containing 95% by weight of a 1:1 mixture of the 1R cis S- and 1S cis R- isomers of alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate.

30 The solvent was evaporated from the filtrate and the residue (2.5kg) was dissolved in triethylamine (3.75 litres), stirred for 21 days at 15°C and treated as above to isolate the white crystalline solid, which amounted to 25g, had m.p. 83.5-85.5°C and contained 95% by weight of a 1:1 mixture of the 1R cis S- and 1S

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cis R- isomers of alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate.

5 Thus in the two treatment steps the 95% pure 1:1 mixture of 1R cis S- and 1S cis R- isomers of alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate was obtained in overall yield of only 65% based on the weight of the amber oil.

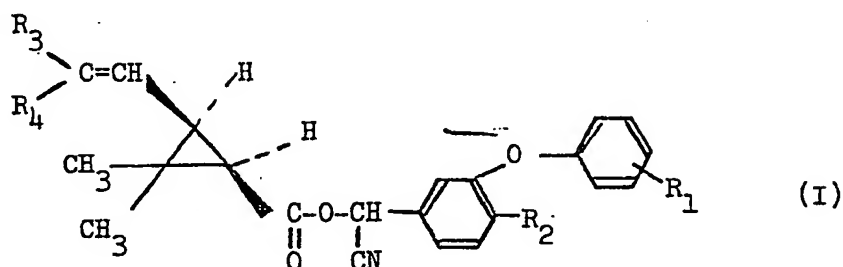
10 Similar experiments in which the amber oil contained 6% and 10% of trans-isomers gave corresponding respective overall yields of 95% pure 1:1 mixtures of 1R cis S- and 1S cis R- isomers of alpha-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate of only 63% and 36% by weight of the amber oils.

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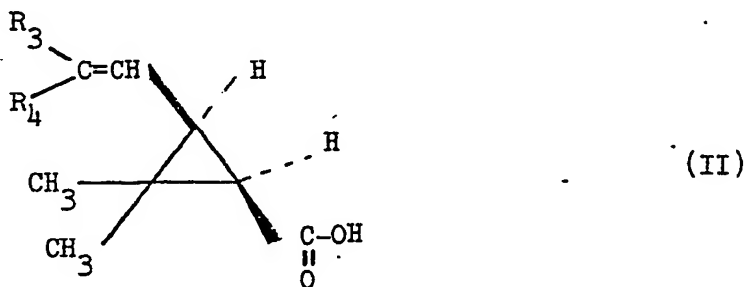
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CLAIMS

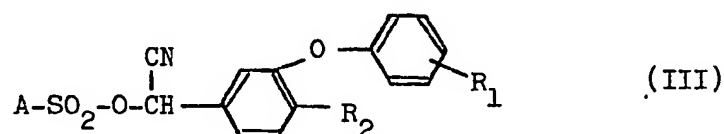
1. A method for preparing a pyrethroid insecticide of general formula:



wherein the two hydrogen atoms on the cyclopropane ring are in the cis- configuration, characterised in that an acid of formula



is neutralised with a water-soluble base and then reacted in the presence of a phase-transfer catalyst with a solution in a substantially water-immiscible organic solvent of an alpha-cyanobenzyl aryl sulphonate of formula:



16.

the substituents in the formulae having the following meanings; A represents an optionally substituted aryl group; each of  $R_1$  and  $R_2$  independently represents a hydrogen or halogen atom; and each of  $R_3$  and  $R_4$  independently represents a chlorine or bromine atom or a methyl group.

2. A method as claimed in claim 1 wherein  $R_1$  and  $R_2$  are both hydrogen atoms and  $R_3$  and  $R_4$  are both chlorine atoms.
3. A method as claimed in claim 1 or 2 wherein A is a tolyl group.
4. A method as claimed in any one of claim 1-3 wherein the phase transfer catalyst is a quaternary ammonium compound or a macrocyclic polyether.
5. A method as claimed in claim 4 wherein the phase transfer catalyst is a tetraalkyl ammonium halide.
6. A method as claimed in any one of the preceding claims wherein the organic solvent is toluene or carbon tetrachloride.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
D,Y	FR-A-2 331 545 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * Claims * & GB - A - 1 540 632  ---	1,4-6	C 07 C 121/75 // C 07 C 143/68 C 07 C 139/00
X,Y	FR-A-2 143 820 (SUMITOMO CHEMICAL COMPANY LTD.) * Claims 1,8,9,14; page 4, line 29 - page 5, line 3 *  ---	1-3,6	
P,X	CHEMICAL ABSTRACTS, vol. 96, no. 5, 1st February 1982, page 613, no. 34668w, Columbus, Ohio, USA & JP - A - 81 81538 (SUMITOMO CHEMICAL CO., LTD.) 03-07-1981 * Abstract *  -----	1-3,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 07 C 121/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26-08-1982	Examiner BERTE M. J.
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